

PATENT SPECIFICATION

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(54) PRODUCTION OF DIHYDROXYARYLSULPHONIUM SALTS

(71) We, J. R. GEIGY A.G., a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns a new process for the production dihydroxyarylsulphonium salts as well as the new products obtained.

For the synthesis of aromatic sulphonium salts, various processes are known which in general, besides the aromatic compound, employ sulphoxides as starting materials. Hitherto, however, there has been no generally applicable method for producing dihydroxyaryl-sulphonium salts of greatly varied type.

A process has now been found which enables these compounds to be obtained in a simple manner with high yields. It is characterized by adding organic sulphides in a strongly acid medium to 1,4-quinones having no substituent in a m-position to a quinone oxygen or to 1,2-quinones having no substituent in p-position to one of the two quinone oxygen functions.

As quinones primarily compounds of the general Formula I



(II)

are used.
In these formulae:

X, Y and Z, independently of each other, represent hydrogen, an alkyl group of from 1 to 18 carbon atoms, a hydroxyl group, a lower alkoxy carbonyl group, a halogen atom, an unsubstituted or substituted phenyl group, or an —SR or —OR group wherein R represents an unsubstituted or substituted alkyl group of from 1 to 18 carbon atoms or an unsubstituted or substituted phenyl group,

or
X and Y together represent a fused ring, preferably an unsubstituted or substituted benzo radical.

The expressions "lower alkyl group", "lower alkoxy group" or "lower alkoxy carbonyl group" indicate an alkyl, alkoxy or alkoxy carbonyl group having 1 to 4 carbon atoms in the alkyl radical.

When X, Y or Z represents an alkyl group of from 1 to 18 carbon atoms, it is an unbranched or branched hydrocarbon chain, e.g. methyl, ethyl, propyl, isopropyl, butyl, pentyl, isopentyl, heptyl, octyl, decyl, dodecyl, hexadecyl or octadecyl.

When X, Y or Z represents a halogen atom, it is for example fluorine, chlorine or bromine; when X, Y or Z represents a substituted phenyl group, suitable non-ionic substituents are, e.g. halogens such as fluorine, chlorine and bromine, nitro groups or lower alkyl groups.

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(I)

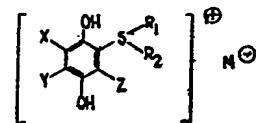
or compounds of the general Formula II

[Price 25p]

- If X, Y or Z is an —SR or —OR group in which R represents a substituted phenyl group, this can contain the usual non-ionic ring substituents such as hydroxyl groups, halogen atoms, e.g. fluorine, chlorine or bromine, nitro groups, lower alkoxy groups, especially, however, lower alkyl groups; when R represents a substituted lower alkyl group, examples of substituents which may be mentioned are carboxyl groups, carboxylic acid ester groups, cyano groups or lower alkoxy groups.
- When X and Y together form a fused ring, suitable examples are homo- or heterocyclic saturated or unsaturated fused rings which can be unsubstituted or substituted, and in case they are aromatic, they can be condensed with other aromatic rings. Preferably X and Y together form an unsubstituted or substituted benzo radical. These fused rings can contain the same non-ionic ring substituents which are given above for R as a substituted phenyl group.
- Especially suited for the process according to the invention are quinones of the general Formula I in which X, Y and Z, independent of one another, represent hydrogen, a lower alkyl group or a halogen atom.
- Examples of such quinones which can be used as starting materials are: 1,2 - benzoquinone, 1,4 - benzoquinone, 5 - methyl - 1,2 - benzoquinone, 2 - methyl - 1,4 - benzoquinone, 2 - butyl - 1,4 - benzoquinone, 2 - dodecyl - 1,4 - benzoquinone, 5 - hexadecyl - 1,2 - benzoquinone, 2 - octadecyl - 1,4 - benzoquinone, 2,5 - dimethyl - 1,4 - benzoquinone, 3,5 - di - tert.butyl - 1,4 - benzoquinone, 2 - isopropyl - 5 - methyl - 1,4 - benzoquinone, 3 - chloro - 1,2 - benzoquinone, 2 - chloro - 1,4 - benzoquinone, 2,5 - di-chloro - 1,4 - benzoquinone, 2,6 - dibromo - 1,4 - benzoquinone, 2 - chloro - 3 - methyl - 1,4 - benzoquinone, 2 - bromo - 6 - methyl - 1,4 - benzoquinone, 2 - phenyl - 1,4 - benzoquinone, 2,5 - diphenyl - 1,4 - benzoquinone, 2 - (4' - bromo) - phenyl - 1,4 - benzoquinone, 2 - (2' - chloro) - phenyl - 1,4 - benzoquinone, 2 - (4' - methyl) - phenyl - 1,4 - benzoquinone, 2 - (3' - or 4' - nitro) - phenyl - 1,4 - benzoquinone, 2,5 - dimethylthio - 2,5 - diethylthio - or 2,5 - dibutylthio - 1,4 - benzoquinone, 2 - octylthio - 1,4 - benzoquinone, 2 - dodecylthio - 1,4 - benzoquinone, 2 - octadecylthio - 1,4 - benzoquinone, 2 - butoxy - 1,4 - benzoquinone, 2,5 - dimethoxy - 1,4 - benzoquinone, 3 - or 5 - hydroxy - 1,2 - benzoquinone, 2 - carboxymethylthio - 1,4 - benzoquinone, 3 - hydroxy - 5 - ethoxy carbonyl - 1,2 - benzoquinone, 2 - cyclohexyl oxycarbonylmethylthio - 1,4 - benzoquinone, 2 - butoxycarbonylmethylthio - 1,4 - benzoquinone, 2 - octadecyloxycarbonylmethylthio - 1,4 - benzoquinone, 2 - cyanoethylthio - 1,4 - benzoquinone, 2,5 - diethoxyethylthio - 1,4 - benzoquinone, 2,5 - diphenoxy - 1,4 - benzoquinone, 2 - phenylthio - 1,4 - benzoquinone, 2,6 - diphenylthio - 1,4 - benzoquinone, 2,5 - diphenylthio - 1,4 - benzoquinone, 2,5 - di - (4' - chloro) - phenylthio - 1,4 - benzoquinone, 2 - (2' - nitro) - phenylthio - 1,4 - benzoquinone, 2 - (4' - methoxy) - phenylthio - 1,4 - benzoquinone, 2 - (4' - butyl) - phenylthio - 1,4 - benzoquinone, 2 - (4' - chloro) - phenylthio - 1,4 - benzoquinone, 2,5 - di - (4' - bromo) - phenoxy - 1,4 - benzoquinone, 2 - (2' - methoxy) - phenoxy - 1,4 - benzoquinone, 2 - (4' - butoxy) - phenoxy - 1,4 - benzoquinone, 2,5 - di - (4' - methyl) - phenoxy - 1,4 - benzoquinone; furthermore 1,2 - naphthoquinone, 1,4 - naphthoquinone, 2 - phenyl - 1,4 - naphthoquinone, 3 - methyl - 1,2 - naphthoquinone, 2 - hydroxy - 1,4 - naphthoquinone, 3 - hydroxy - 1,2 - naphthoquinone, 2 - chloro - 1,4 - naphthoquinone, 2 - methyl - 1,4 - naphthoquinone, 2 - ethyl - 1,4 - naphthoquinone, 6 - hydroxy - 1,2 - naphthoquinone, 6 - hydroxy - 1,4 - naphthoquinone, 5,8 - dihydroxy - 1,4 - naphthoquinone, 5 - or 6 - chloro - 1,4 - naphthoquinone, 3,6 - dibromo - 1,4 - naphthoquinone, 8 - nitro - 1,4 - naphthoquinone, 2,5 - dimethyl - 1,4 - naphthoquinone, 2 - methyl - 5 - hydroxy - 1,4 - naphthoquinone, quinolinequinone - 5,8 or 1,4 - anthraquinone.
- As organic sulphides in the process according to the invention, preferably those of the general formula III
- R_1-S-R_2 (III)
- are used in which
- R_1 represents an unsubstituted or substituted, saturated or unsaturated acyclic or cyclic hydrocarbon radical, preferably an unsubstituted or substituted alkyl group having at most 12 carbon atoms in the main chain, a propenyl group or an unsubstituted or substituted phenyl group, and
- R_2 represents an unsubstituted or substituted, saturated or unsaturated aliphatic or cycloaliphatic hydrocarbon radical, preferably an unsubstituted or substituted alkyl group having at most 12 carbon atoms in the main chain, or
- R_1 and R_2 together represent a chain of 4 to 6 methylene groups, optionally including another hetero atom in the chain and optionally including lower alkyl substituent groups, such hetero atoms being preferably sulphur and oxygen.
- Examples of R_1 and R_2 as unsubstituted alkyl groups having at most 12 carbon atoms are: methyl, ethyl, propyl, isopropyl, butyl, pentyl, isopentyl, heptyl, octyl, decyl or dodecyl groups. Examples of substituents in

- such alkyl groups are, for example: phenyl groups, halogens such as chlorine or bromine, hydroxyl groups, alkoxy groups of 1 to 12 carbon atoms, phenoxy groups the phenyl radical of which can be substituted by chlorine or bromine, lower hydroxyalkoxy or alkoxyalkoxy groups, as well as lower alkylthio groups which are separated by at least 3 carbon atoms from the sulphur atom in the general Formula III.
- When R₁ represents a substituted phenyl group, it can be substituted by the usual non-ionic ring substituents such as the halogens fluorine, chlorine or bromine, in particular, however, by lower alkyl groups or alkoxy groups; advantageously, however, the phenyl radical is unsubstituted.
- Especially advantageous for the process according to the invention are organic sulphides of the general Formula III in which, of R₁ and R₂, at least one R represents a lower alkyl group, or in which R₁ and R₂ together represent a chain of 4 to 6 further methylene groups.
- Examples of organic sulphides which are suitable as starting materials are: dimethyl sulphide, diethyl sulphide, dipropyl sulphide, diisopropyl sulphide, dibutyl sulphide, diisobutyl sulphide, dipentyl sulphide, diisopentyl sulphide, diheptyl sulphide, dioctyl sulphide, didecyl sulphide, didodecyl sulphide, methyl isobutyl sulphide, methyl pentyl sulphide, methyl hexyl sulphide, ethyl octyl sulphide, methyl decyl sulphide, methyl dodecyl sulphide, dibenzyl sulphide, methyl benzyl sulphide, (3'-methyl) - benzyl - (4' - methoxy) - benzyl sulphide, ethyl phenethyl sulphide, 3,3' - dichlorodipropyl sulphide, di - ω - hydroxyethyl sulphide, di - ω - hydroxybutyl sulphide, di - ω - hydroxyhexyl sulphide, methyl - ω - hydroxyethyl sulphide, methyl - ω - hydroxybutyl sulphide, dimethoxy methyl or dibutoxy methyl sulphide, dimethoxy - , diethoxy - , dipropoxy - , diisopropoxy - , dibut oxy - or didodecyloxy - ethyl sulphide, 3 - chloropropyl methyl sulphide, dimethoxybutyl sulphide, methyl - ω - methoxyethyl sulphide, methyl - ω - ethoxyethyl sulphide, didodecyl-oxypropyl sulphide, diphenoxyethyl sulphide, methyl - (4 - methylthio) - butyl sulphide, methyl - (6 - methylthio) - hexyl sulphide, ethyl - (6 - ethylthio) - hexyl sulphide, butyl - (6 - butylthio) - hexyl sulphide, methyl allyl sulphide, methyl prop - 1 - en sulphide and methyl hex - 1 - en sulphide; in addition phenylmethyl sulphide, phenylethyl sulphide, phenylbutyl sulphide, phenylisobutyl sulphide, phenylpentyl sulphide, (2 - , 3 - or 4 - methylphenyl - 1) - methyl or ethyl sulphide, 4 - ethoxyphenyl - 1 methyl sulphide, 2 - chlorophenyl - 1 - methyl sulphide, 2 - or 4 - bromophenyl - 1 - methyl sulphide and 2 - chlorophenyl - 1 - methyl sulphide as well as tetrahydrothiophene, 2 - methyl - , 3 - methyl - 65 or 3 - ethyl - tetrahydrothiophene, 3,4 - dimethyltetrahydrothiophene, 2,3 - dimethyltetrahydrothiophene, tetrahydrothiopyran, hexahydrothiepine, 1,3 - or 1,4 - dithiane and 1,4 - oxathiane, methyl cyclopropyl sulphide, methyl cyclopentyl sulphide, methyl cyclohexyl sulphide, methyl cyclooctyl sulphide and dicyclohexyl sulphide.
- The compounds which are employed according to the invention as starting materials are known or can be produced by known methods.
- The reaction of the starting materials in a strongly acid medium is advantageously performed at temperatures of -40 to 50°C, preferably at -15 to 25°C and the acids used can be Brønsted-Lowry acids or Lewis acids.
- Examples of Brønsted-Lowry acids, which can give up a proton to a base and therefore serve as proton donor, usable in the process according to the invention are the following: sulphuric acid, pyrosulphuric acid, phosphoric acid, polyphosphoric acid, hydrofluoric acid, tetrafluoroboric acid, formic acid, acetic acid, trifluoroacetic acid, oxalic acid, perchloric acid 90 or p-toluene sulphonic acid.
- Examples of Lewis acids, which can take up an electron pair and therefore serve as electron acceptor, usable in the process according to the invention are the following: aluminum chloride, aluminum bromide, boron fluoride, phosphorus trichloride, phosphorus oxychloride, antimony pentafluoride or pentachloride, iron(III) chloride or tin(IV) chloride.
- Preferably as strongly acid medium an aqueous or aqueous-organic solution is employed having a pH value below 1.0, or an inorganic or organic acid is employed having a pK value in water of less than 4.8, or an organic solvent is employed which is inert under the reaction conditions, e.g. acetic acid, propionic acid, acetic acid anhydride, sulpholane, nitromethane, nitrobenzene or nitrotoluene; or a mixture of such solvents is employed, containing a Brønsted-Lowry acid having a pK value in water of less than 4.8, or containing a Lewis acid. Examples of suitable solvent mixtures to produce in combination with a corresponding Brønsted-Lowry acid a strongly acid aqueous-organic solution having a pH value below 1, are the following: mixtures of water with acetic acid, propionic acid, sulpholane, methanol, ethanol, acetone or methyl ethyl ketone.
- Particularly preferred as strongly acid medium is aqueous sulphuric acid, especially 60 to 85% aqueous sulphuric acid; furthermore aqueous phosphoric acid, aqueous perchloric acid or aqueous hydrofluoric acid as well as polyphosphoric acid can also often be used advantageously.

- For the reaction, equivalent amounts of the starting materials are used, or a 5 to 10% excess of an organic sulphide is used. Organic sulphides having a second thio function, where-
 5 by these two thio functions must be separated by at least 3 carbon atoms from each other, can react with two molecules of a quinone, i.e. 1 mol of such a bisthio compound reacts with 2 moles of an appropriate quinone.
- 10 The acid must also be present in at least an equimolar amount; preferably, however, an excess of acid is employed, especially when the reaction is performed in the presence of water or solvents containing water.
- 15 In practice, the reaction can be performed so that the quinone is mixed with the organic sulphide and introduced into the acid medium; the quinone can, however, also be present in the acid medium and the organic sulphide then added; or, finally, the organic sulphide can be present in the acid medium and then the quinone added thereto.
- 20 To isolate the end products, various methods can be used, depending on the reaction medium and the solubility properties of the compounds. For example, the dihydroxyaryl sulphonium salts can be precipitated directly from the acidic aqueous solution by the addition of anions with which they form poorly soluble
 25 salts, such as reineckates, thiocyanates or picrates. When the reaction is performed in aqueous sulphuric acid or phosphoric acid, the reaction medium can, after dilution with ice water, be neutralized with calcium hydroxide; after separation of the calcium sulphate or calcium phosphate which precipitates, the solution is acidified with a volatile acid, for example hydrochloric acid or hydrobromic acid, whereupon, after removal of the solvent by
 30 distillation, the sulphonium compound is obtained as the corresponding salt, e.g. as the chloride or bromide. In case the reaction is performed in a non-water-miscible solvent containing acid, water can be added to the reaction mixture, thus obtaining transfer of the sulphonium compound formed into the aqueous phase which can be appropriately further processed. Frequently, when the sulphuric or phosphoric acid solution is diluted
 35 with ice water, the dihydroxsulphonium salts precipitate directly as the sulphates or phosphates. Preferably, when using aqueous acids, these are neutralized with an alkali hydroxide, e.g. sodium or potassium hydroxide and then
 40 reacidified with an excess of a hydrohalic acid such as hydrochloric or hydrobromic acid, whereby the corresponding halide precipitates.
 45 The addition at 0 to 5°C of an equimolar amount of the sulphide to a suspension of the quinone in the eightfold amount by weight of 60—70% aqueous sulphuric acid has proved to be an especially suitable process for the production of the dihydroxyaryl sulphonium
 50 salts. Depending upon the reactivity of the components, the reaction time is usually from about 15 minutes to 6 hours.
- 55 According to a further aspect of the present invention, there is provided a novel compound having the formula
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wherein

X, Y and Z independently of each other, represent hydrogen, an alkyl group of from 1 to 18 carbon atoms, a hydroxyl group, a halogen atom, and unsubstituted or substituted phenyl group, or an —SR or —OR group wherein R represents an unsubstituted or substituted alkyl group of from 1 to 18 carbon atoms or an unsubstituted or substituted phenyl group, provided that if 2 of the substituents X, Y and Z are other than hydrogen, the said substituents which are other than hydrogen must be identical and that if 2 of X, Y and Z are hydrogen, these are represented by X and Z, or X and Y together represent a fused ring,

R₁ represents

- (i) an unsubstituted or substituted unsaturated acyclic hydrocarbon radical or
- (ii) a substituted saturated acyclic hydrocarbon radical or
- (iii) a phenyl radical substituted by lower alkoxy groups or
- (iv) a cycloaliphatic hydrocarbon radical;

R₂ represents an unsubstituted or substituted saturated or unsaturated aliphatic or cycloaliphatic hydrocarbon radical

or
 R₁ represents a phenyl radical or a phenyl radical substituted by halogen or lower alkyl and R₂ represents an unsubstituted alkyl radical of at least 2 carbon atoms;

or
 if R₁ and R₂ represent an unsubstituted alkyl radical of from 1 to 4 carbon atoms, said radicals are not identical;

or
 if of X, Y and Z at least one is not hydrogen, R₁ and R₂ represent an alkyl radical of from 1 to 4 carbon atoms, or R₁ represents an unsubstituted or substituted phenyl radical and R₂ represents a methyl group;

or
 R₁ and R₂ together represent a chain of 4 to 6 methylene groups, optionally including another hetero atom in the chain and optionally including lower alkyl substituent groups;

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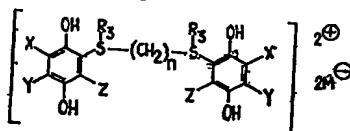
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and M^{\ominus} represents a monovalent anion;
or
a compound having the formula



5 wherein

X, Y and Z, independently of each other represent hydrogen, lower alkyl or halogen, provided that if 2 of the substituents X, Y and Z are other than hydrogen, the two substituents

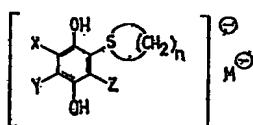
10 which are other than hydrogen must be identical and that if 2 of X, Y and Z are hydrogen, these are represented by X and Z,
or

X and Y together represent a fused ring;

15 R₃ represents lower alkyl;
n represents an integer ranging from 3 to 6, and

M^{\ominus} represents a monovalent anion.

A preferred class of compounds provided
20 by the present invention in an easy way corresponds to the formula



wherein

25 X, Y and Z represent hydrogen or
X and Y together represent a fused benzo radical and
Z is hydrogen;
n represents an integer ranging from 4 to 6; and

30 M^{\ominus} represents a monovalent anion.

The sulphonium salts produced according to the new process are, conforming to the nature of salts, solid substances, which, however, in many cases cannot be crystallized. At high temperatures they melt usually at an indefinite melting point with decomposition. If possible, it is advantageous to characterize them as halide, thiocyanate, perchlorate, picrate or reineckate. Most of the sulphonium salts, in particular, e.g. the halides or sulphates are very readily water-soluble; frequently, however, they are also soluble in ethanol, acetone or chloroform. As reactive compounds, dihydroxyaryl sulphonium salts are valuable intermediate products, for example in the dye-stuff industry, in some cases they exhibit fungicidal or bactericidal effects.

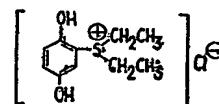
35 The advantages of the new process for the production of dihydroxyaryl sulphonium salts lie in its wide range of application, by which compounds which were hitherto inaccessible or only difficultly accessible can be synthesized in a simple manner. Moreover, it is surprising

that in spite of the strongly acid conditions, practically no byproducts are formed and the yields are therefore usually very high.

55 The following examples illustrate the invention. The temperatures are given in degrees centigrade.

EXAMPLE 1

10.8 g of finely pulverized 1,4-benzoquinone are suspended at -5 to 0° in 40 ml of 70% aqueous sulphuric acid, a part of which dissolves, and then while stirring well 9.4 g of diethyl sulphide are added. The reaction is allowed to continue with stirring until the originally dark solution becomes light and a sample dissolves clear and colourless in water. 100 ml of water are then added dropwise to the reaction mixture, continuing to keep the temperature at 0°. The solution is then neutralized, while cooling, with 30% aqueous sodium hydroxide solution, treated with 100 ml of concentrated hydrochloric acid and kept for several hours at 0° with stirring. The crystalline precipitate is then removed by filtration and dried in vacuum. 22.0 g (93% of theory) of an almost colourless sulphonium salt of the formula



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are obtained. After recrystallizing twice at 60° from 2% aqueous or alcoholic hydrochloric acid, it exhibits a melting point of 143° (decomposition).

85 The corresponding bromide is obtained in an analogous manner when the hydrochloric acid in the above example is replaced by an equivalent amount of hydrobromic acid. By using instead of 40 ml of 70% aqueous sulphuric acid an equal volume of 85% phosphoric acid, 85% formic acid, 70% perchloric acid or 66% hydrofluoric acid and otherwise repeating the procedure as given in the above example, the same compound of the corresponding salt is obtained in similar yield.

90 When the starting materials given in Example 1 are replaced by the equivalent amounts of the quinones given in Column 2 of Table 1 and of the sulphides given in Column 3, and the procedure of the example is followed, the temperatures of the reactions lying between -15 and +20°, the corresponding dihydroxy sulphonium salts given in Column 4 are obtained, the melting points of those which can be determined being given in Column 5.

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110 In case the sulphates which form in the reaction in sulphuric acid are poorly soluble, they can, after dilution of the reaction solution with ice water, be removed directly by filtration.

TABLE 1

Example No.	quinone	sulphide	dihydroxysulphonium salt	melting point
2		$S(C_2H_5)_2$		145°
3				
4		$S(CH_3)_2$		
5				172°
6		$S(CH_2CH_2OCH(CH_3)_2)_2$		
7		$S(CH(CH_3)_2)_2$		

TABLE 1 Continued

Example No.	quinone	sulphide	dihydroxysulphonium salt	m.p.
8				
9		$S(CH_2CH_2CH_3)_2$		145°
10		$S(CH_2CH_2CH_2CH_3)_2$		132°
11		$S(CH_2CH_2CH_2Cl)_2$		
12		$S(C_2H_5)_2$		
13				

TABLE 1 Continued

Example No.	quinone	sulphide	dihydroxysulphonium salt	m.p.
14				
15		$S(CH_3)_2$		
16		$S(CH_3)_2$		
17				119°
18		$S(CH_2CH_2OCH_2CH_3)_2$		116°
19		$CH_3S\text{---}C_6H_5$		105°

TABLE 1 Continued

Example No.	quinone	sulphide	dihydroxysulphonium salt	m.p.
20		$\text{CH}_3\text{-S-} \text{C}_6\text{H}_4\text{-CH}_3$	$\left[\text{C}_6\text{H}_4\text{-S}(\text{CH}_3)\text{-C}_6\text{H}_4\text{-CH}_3 \right]^{+}\text{Br}^{-}$	
21		$\text{CH}_3(\text{CH}_2)_4\text{-S-} \text{C}_6\text{H}_5$	$\left[\text{C}_6\text{H}_4\text{-S}(\text{CH}_3(\text{CH}_2)_4\text{-C}_6\text{H}_5) \right]^{+}\text{Cl}^{-}$	
22		$\text{S}(\text{CH}_3)_2 < \text{CH}_3$ $(\text{CH}_2)_4\text{CH}_3$	$\left[\text{C}_6\text{H}_4\text{-S}(\text{CH}_3)_2(\text{CH}_2)_4\text{CH}_3 \right]^{+}\text{Cl}^{-}$	
23		$\text{S}(\text{CH}_3)_2$	$\left[\text{C}_6\text{H}_4\text{-S}(\text{CH}_3)_2 \right]^{+}\text{Cl}^{-}$	
24		$\text{S}(\text{CH}_3)_2 < \text{CH}_3$ $(\text{CH}_2)_{11}\text{CH}_3$	$\left[\text{C}_6\text{H}_4\text{-S}(\text{CH}_3)_2(\text{CH}_2)_{11}\text{CH}_3 \right]^{+}\text{Br}^{-}$	
25		$\text{S}(\text{CH}_3)_2 < \text{CH}_3$ $\text{CH}_2\text{-CH=CH}_2$	$\left[\text{C}_6\text{H}_4\text{-S}(\text{CH}_3)_2\text{-CH}_2\text{-CH=CH}_2 \right]^{+}\text{Cl}^{-}$	

TABLE 1 Continued

Example No.	quinone	sulphide	dihydroxysulphonium salt	m.p.
26		$S(CH_3)_2$	$\left[\text{C}_6\text{H}_4\text{C}_6\text{H}_3(\text{NO}_2)\text{CO}_2\text{S}(\text{CH}_3)_2 \right]^{+}\text{HSO}_4^-$	
27		$\text{S}^{\text{H}}\text{S}$	$\left[\text{C}_6\text{H}_4\text{C}_6\text{H}_3(\text{Br})\text{CO}_2\text{S}^{\text{H}}\text{S} \right]^{+}\text{ClO}_4^-$	
28		$\text{S}^{\text{H}}\text{S}$	$\left[\text{C}_6\text{H}_4\text{C}_6\text{H}_3(\text{Cl})\text{CO}_2\text{S}^{\text{H}}\text{S} \right]^{+}\text{ClO}_4^-$	
29		$S(C_2H_5)_2$	$\left[\text{C}_6\text{H}_4\text{C}_6\text{H}_3(\text{CH}_3)_2\text{CO}_2\text{S}(\text{C}_2\text{H}_5)_2 \right]^{+}\text{Br}^-$	
30		$\text{S}^{\text{H}}\text{S}$	$\left[\text{C}_6\text{H}_4\text{SC}_6\text{H}_4\text{C}_6\text{H}_3(\text{C}_6\text{H}_5)\text{CO}_2\text{S}^{\text{H}}\text{S} \right]^{+}\text{Cl}^-$	126°
31		$\text{S}^{\text{H}}\text{S}$	$\left[\text{C}_6\text{H}_4\text{SC}(\text{CH}_3)_2\text{C}_6\text{H}_3(\text{C}_6\text{H}_5)\text{CO}_2\text{S}^{\text{H}}\text{S} \right]^{+}\text{Cl}^-$	94°
32		$\text{S}^{\text{H}}\text{S}$	$\left[\text{C}_6\text{H}_4\text{S}(\text{CH}_2)_{17}\text{CH}_3\text{C}_6\text{H}_3(\text{C}_6\text{H}_5)\text{CO}_2\text{S}^{\text{H}}\text{S} \right]^{+}\text{Br}^-$	

TABLE 1 Continued

Example No.	quinone	sulphide	dihydroxysulphonium salt	m.p.
33		$\text{CH}_3\text{-S}-\text{C}_2\text{H}_4$	$\left[\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_3\text{CO} \\ \\ \text{OH} \end{array} - \text{S}-\text{C}_2\text{H}_4 - \text{NO}_2\text{-C}_6\text{H}_3\text{NO}_2 \right]^\oplus \text{HSO}_4^-$	
34		$\text{CH}_3\text{-S}-\text{C}_2\text{H}_4$	$\left[\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_3\text{CO} \\ \\ \text{OH} \end{array} - \text{S}-\text{C}_2\text{H}_4 - \text{Cl} \right]^\oplus \text{Cl}^-$	
35		$\text{CH}_3\text{-S}-\text{C}_2\text{H}_4$	$\left[\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_3\text{CO} \\ \\ \text{OH} \end{array} - \text{S}-\text{C}_2\text{H}_4 - \text{C}_6\text{H}_5 \right]^\oplus \text{HSO}_4^-$	
36		$\text{CH}_3\text{-S}-\text{C}_2\text{H}_4\text{OH}$	$\left[\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_3\text{CO} \\ \\ \text{OH} \end{array} - \text{S}-\text{C}_2\text{H}_4 - \text{CH}_2\text{CH}_2\text{OH} \right]^\oplus [\text{O}(\text{NH}_3)_2\text{SCN}_4]^-$	134°
37		$\text{CH}_3\text{-S}-\text{C}_2\text{H}_4$	$\left[\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_3\text{CO} \\ \\ \text{OH} \end{array} - \text{S}-\text{C}_2\text{H}_4 - \text{CH}_2-\text{CH}(\text{CH}_3)-\text{C}_2\text{H}_4 \right]^\oplus \text{Cl}^-$	125°
38		$\text{S}(\text{C}_2\text{H}_5)_2$	$\left[\begin{array}{c} \text{Br-C}_6\text{H}_4-\text{O} \\ \\ \text{C}_6\text{H}_3\text{CO} \\ \\ \text{Br-C}_6\text{H}_4-\text{O} \end{array} - \text{S}-\text{C}_2\text{H}_4 - \text{O}(\text{C}_6\text{H}_4-\text{Br})_2 \right]^\oplus \text{ClO}_4^-$	
39		S	$\left[\begin{array}{c} \text{Cl-C}_6\text{H}_4-\text{S} \\ \\ \text{C}_6\text{H}_3\text{CO} \\ \\ \text{Cl-C}_6\text{H}_4-\text{S} \end{array} - \text{S}-\text{C}_2\text{H}_4 - \text{O} \right]^\oplus \text{Cl}^-$	116°
40		$\text{CH}_3\text{-CH}_2\text{-CH}(\text{CH}_3)_2$	$\left[\begin{array}{c} \text{CH}_3(\text{CH}_2)_2-\text{C}_6\text{H}_4-\text{S} \\ \\ \text{C}_6\text{H}_3\text{CO} \\ \\ \text{CH}_3(\text{CH}_2)_2-\text{C}_6\text{H}_4-\text{S} \end{array} - \text{S}-\text{C}_2\text{H}_4 - \text{CH}_2-\text{CH}(\text{CH}_3)_2 \right]^\oplus \text{HSO}_4^-$	

TABLE 1 Continued

Example No.	quinone	sulphide	dihydroxysulphonium salt	m.p.
41		$\text{S}(\text{CH}_2\text{CH}_2\text{OCH}_3)_2$	$\left[\text{C}_6\text{H}_4\text{O}_2\text{--O}(\text{CH}_2)_5\text{CH}_3 \right]_{\text{HSO}_4^-}$	
42		$\text{S}(\text{CH}_3)_2$	$\left[\text{C}_6\text{H}_4\text{O}_2\text{--O}(\text{CH}_2)_5\text{CH}_3 \right]_{\text{Br}}$	
43		$\text{S}(\text{CH}_2\text{CH}_2\text{OCH}_3)_2$	$\left[\text{C}_6\text{H}_4\text{O}_2\text{--O}(\text{CH}_2)_5\text{CH}_3 \right]_{\text{SCN}^-}$	
44			$\left[\text{C}_6\text{H}_4\text{O}_2\text{--O}(\text{CH}_2)_5\text{CH}_3 \right]_{\text{Cl}^-}$	155°
45			$\left[\text{C}_6\text{H}_4\text{O}_2\text{--O}(\text{CH}_2)_5\text{CH}_3 \right]_{\text{Cl}^-}$	124°
46		$\text{OCH}_3\text{--S}(\text{CH}_2\text{CH}_2\text{OCH}_3)\text{OC}_2\text{H}_5$	$\left[\text{C}_6\text{H}_4\text{O}_2\text{--O}(\text{CH}_2)_5\text{CH}_3 \right]_{\text{SO}_4^-}$	
47		$\text{S}(\text{C}_2\text{H}_5)_2$	$\left[\text{C}_6\text{H}_4\text{O}_2\text{--O}(\text{CH}_2)_5\text{CH}_3 \right]_{\text{Br}}$	
48		$\text{S}(\text{CH}_2\text{CH}_2\text{OCH}_3)_2$	$\left[\text{C}_6\text{H}_4\text{O}_2\text{--O}(\text{CH}_2)_5\text{CH}_3 \right]_{\text{HSO}_4^-}$	

TABLE 1 Continued

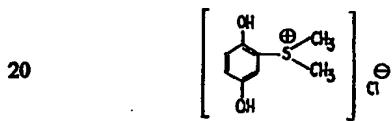
Example No.	quinone	sulphide	dihydroxysulphonium salt	m.p.
49				
50				150°
51				136°
52		$\text{CH}_3-\text{S}-(\text{CH}_2)_4-\text{S}-\text{CH}_3$		
53		$\text{CH}_3-\text{S}-(\text{CH}_2)_6-\text{S}-\text{CH}_3$		154°
54		$\text{C}_4\text{H}_9-\text{S}-(\text{CH}_2)_6-\text{S}-\text{C}_4\text{H}_9$		
55		$\text{C}_2\text{H}_5-\text{S}-(\text{OH}_2)_6-\text{S}-\text{C}_2\text{H}_5$		
56		$\text{CH}_3-\text{S}-(\text{CH}_2)_6-\text{S}-\text{CH}_3$		

TABLE 1 Continued

Example No.	quinone	sulphide	dihydroxysulphonium salt	m.p.
57				
58		$S(C_2H_5)_2$		
59				133°
60		$CH_3CH_2S-C_6H_5$		
61		$CH_3CH_2CH_2-S-CH_3$		
62		$C_6H_5-S-C_6H_5$		

EXAMPLE 63

- 21.6 g of pulverized 1,4-benzoquinone are suspended at -5° in 60 ml of 70% aqueous sulphuric acid, a part of which dissolves, and then 12.8 g of dimethyl sulphide are added dropwise during 30 minutes. The originally yellow-brown reaction mass becomes light in colour after stirring for 2 hours at 0° , and 200 ml of water is slowly added with cooling.
- 10 This solution is adjusted with cooling to a pH value of about 7 with 30% aqueous sodium hydroxide solution, and then 200 ml of concentrated hydrochloric acid are added. After the addition of 40 g of NaCl, the product is allowed to crystallize while cooling and stirring for several hours; the product is then removed by filtration and dried in vacuum. 38 g (92% of theory) of a sulphonium salt of the formula



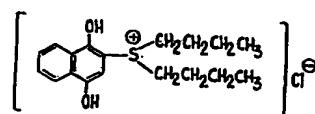
having a melting point of 137—138° (decomposition), are obtained.

The melting point of the product, recrystallized from a little 3% hydrochloric acid at 25 60° , is 142—143° (decomposition).

EXAMPLE 64

- 15.8 g of finely pulverized 1,4-naphthoquinone are suspended at 0 to 5° in 40 ml of 80% aqueous sulphuric acid, a part of which 30 dissolves, and then, while stirring well, 14.6 g of dibutyl sulphide are added. While stirring at 0 to 5° , the reaction is allowed to continue to completion for 5 more hours. 100 ml of water are then added dropwise to the reaction mixture, continuing to keep the temperature between 0 and 5° . The solution is then neutralized with 30% aqueous sodium hydroxide solution while cooling and then 100 ml of concentrated hydrochloric acid are 40 added. The temperature is kept at 0° with

stirring for about 12 hours, the precipitated product is removed by filtration and dissolved in 120 ml of methanol/water (4:1). To this warm, filtered solution, 50 ml of 4% aqueous hydrochloric acid are added and allowed to crystallize with cooling. The sulphonium salt is removed by filtration and dried in vacuum. As end product, a compound of the formula



50 having a melting point of 132° (decomposition), is obtained. When in the procedure described, the neutralized reaction solution is not reacidified with hydrochloric acid, but is diluted to its double volume with water and treated with a saturated aqueous solution of Reinecke's salt ($\text{NH}_4[\text{Cr}(\text{NH}_3)_5(\text{SCN})_4]$), then 50.8 g (89% of theory) of the reineckate of the above sulphonium compound (m.p. 77—80°) are obtained.

55 The corresponding bromide is obtained analogously when the procedure of the above example is followed, but the hydrochloric acid is replaced by the equivalent amount of hydrobromic acid.

60 When the starting materials given in Example 64 are replaced by the equivalent amounts of the quinones given in Column 2 of Table 2 and of the sulphides given in Column 3, and the procedure of the example is followed, the temperatures of the reactions lying between -5 and $+25^{\circ}$, the corresponding dihydroxy sulphonium salts given in Column 4 are obtained, the melting points of those which can be determined being given in Column 5.

65 In case the sulphates which form in the reaction in sulphuric acid are poorly soluble, they can, after dilution of the reaction solution with ice water, be removed directly by filtration.

50

55

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75

80

TABLE 2

Example No.	quinone	sulphide	dihydroxysulphonium salt	m.p.
65		$S(CH_2CH_2CH_2CH_2)_2$		141°
66				
67		$S((CH_2)_7CH_3)_2$		
68		$S(C_2H_5)_2$		136°
69		$CH_2CH_2OCH_3$		
70		$S(CH_2CH_2O(CH_2)_{11}CH_3)_2$		

TABLE 2 Continued

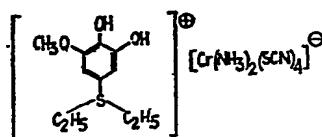
Example No.	quinone	sulphide	dihydroxysulphonium salt	m.p.
71				
72				
73				120°
74				119°
75		$S(C_2H_5)_2$		
76				
77		$CH_3S-C_6H_5$		

TABLE 2 Continued

Example No.	quinone	sulphide	dihydroxysulphonium salt	m.p.
78		S(CH ₃) ₂	[A quinone ring with hydroxyl groups at positions 3 and 4, and a methylsulfide group (-S(CH3)2) at position 2. The cation is enclosed in brackets with a superscript +, and the anion is H2PO4^2-."/>	
79		S	[A dioxin ring with phenyl groups at positions 2 and 5, and hydroxyl groups at positions 3 and 4. The cation is enclosed in brackets with a superscript +, and the anion is HSO4^-."/>	106°
80		S(CH ₂ CH ₂ OH) ₂	[A quinone ring with hydroxyl groups at positions 3 and 4, and a diethanolamido group (-S(CH2CH2OH)2) at position 2. The cation is enclosed in brackets with a superscript +, and the anion is Br^-."/>	
81		S	[A quinone ring with hydroxyl groups at positions 3 and 4, and a thiophene ring at position 2. The cation is enclosed in brackets with a superscript +, and the anion is SCN^-."/>	106°

EXAMPLE 82

To a suspension of 6 g AlCl₃ in 50 ml dry methylene chloride is added, while stirring well, dropwise at -15° a solution of 4.2 g of 3-methoxy-*o*-benzoquinone and 3.5 ml of diethyl sulphide in 100 ml dry methylene chloride. The reaction mixture is kept for 30 minutes at room temperature and then poured into 200 ml of ice water. After evaporating the aqueous solution the sulphonium salt may be isolated as reineckeate by adding a saturated aqueous solution of Reinecke's salt, 11.5 g (69% of theory) of a sulphonium salt of the formula



are obtained. The melting point of the product,

recrystallized twice from 30% aqueous ethanol, is 163-165°. If in the above example instead of the Reinecke's salt an aqueous solution of picric acid is used, the corresponding picrate is obtained which melts at 169-170°.

20

Using instead of 6 g AlCl₃, equimolar amounts of AlBr₃, BF₃, or FeCl₃ and otherwise proceeding as indicated in the example, the corresponding sulphonium salts are obtained in good yields.

25

Instead of methylene chloride also the same amounts of diethyl ether, nitrobenzene or carbon tetrachloride may be used as solvent.

30

When the starting materials given in Example 82 are replaced by the equivalent amounts of the quinones given in Column 2 of Table 3 and of the sulphides given in Column 3, and the procedure of the example is followed, the corresponding dihydroxysulphonium salts given in Column 4 are obtained.

35

TABLE 3

Example No.	quinone	sulphide	dihydroxysulphonium salt
83			
84		$S(CH_3)_2$	
85		$S(C_2H_5)_2$	
86			
87			
88		$S(CH_3)_2$	
89		$S(CH_3)_2$	
90			

WHAT WE CLAIM IS:—

1. Process for the production of dihydroxy-
aryl sulphonium salts, characterized by adding
organic sulphides in a strongly acid medium to
5 1,4-quinones having no substituent in m-posi-
tion to a quinone oxygen or to 1,2-quinones
having no substituent in p-position to one of
the two quinone oxygen functions.
2. Process according to Claim 1, character-
10 ized by employing as quinone, a compound of
the general Formula I



(I)

wherein

- X, Y and Z, independently of each other,
15 represent hydrogen, an alkyl group of from 1
to 18 carbon atoms, a hydroxyl group, a
halogen atom, an unsubstituted or substituted
phenyl group, or an —SR or —OR group
wherein R represents an unsubstituted or sub-
20 stituted alkyl group of from 1 to 18 carbon
atoms or an unsubstituted or substituted phenyl
group, or

X and Y together represent a fused ring.

3. Process according to Claim 2, character-
25 ized by employing a compound of the general
Formula I in which X and Y together repre-
sent an unsubstituted or substituted benzo
radical.

4. Process according to Claim 1, character-
30 ized by employing as quinone, a compound
of the general Formula II



(II)

wherein

- X, Y and Z, independently of each other,
35 represent hydrogen, an alkyl group of from 1
to 18 carbon atoms, a hydroxyl group, a
lower alkoxy or lower alkoxycarbonyl group
or a halogen atom, or

X and Y together represent a fused ring.

- 40 5. Process according to Claim 4, character-
ized by employing a compound of the general
Formula II in which X and Y together repre-
sent an unsubstituted or substituted benzo
radical.

- 45 6. Process according to Claim 1, character-
ized by employing as organic sulphide, a com-
pound of the general Formula III



wherein

- 50 R₁ represents an unsubstituted or sub-

stituted, saturated or unsaturated acyclic or
cyclic hydrocarbon radical, and

R₂ represents an unsubstituted or sub-
stituted, saturated or unsaturated aliphatic or
cycloaliphatic hydrocarbon radical,
55 or R₁ and R₂ together represent a chain of
4 to 6 methylene groups, optionally including
another hetero atom in the chain and option-
ally including lower alkyl substituent groups.

60 7. Process according to Claim 6, character-
ized by employing a compound of the general
Formula III in which

R₁ represents an unsubstituted or substituted
alkyl group having at most 12 carbon atoms in
the main chain, a propenyl group, or an un-
substituted or substituted phenyl group, and

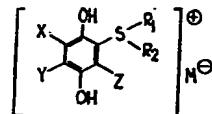
R₂ represents an unsubstituted or substituted
alkyl group having at most 12 carbon atoms in
the main chain.

70 8. Process according to Claim 1, character-
ized by employing as strongly acid medium
an aqueous or aqueous-organic solution having
a pH value below 1.0.

75 9. Process according to Claim 1, character-
ized by employing as strongly acid medium an
inorganic or organic acid having a pK value
in water of less than 4.8.

80 10. Process according to Claim 1, character-
ized by employing as strongly acid medium
an organic solvent which is inert under the
reaction conditions, containing a Brønsted-
Lowry acid having a pK value in water of less
than 4.8, or containing a Lewis acid.

11. Compounds of the formula



85

wherein

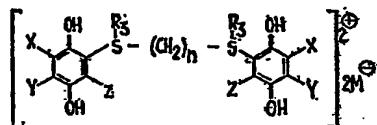
X, Y and Z independently of each other,
90 represent hydrogen, an alkyl group of from 1
to 18 carbon atoms, a hydroxyl group, a
halogen atom, and unsubstituted or substituted
phenyl group, or an —SR or —OR group
wherein R represents an unsubstituted or sub-
95 stituted alkyl group of from 1 to 18 carbon
atoms or an unsubstituted or substituted phenyl
group, provided that if 2 of the sub-
stituents X, Y and Z are other than hydrogen,
the said substituents which are other than
hydrogen must be identical and that if 2 of
X, Y and Z are hydrogen, these are repre-
100 sented by X and Z, or X and Y together repre-
sent a fused ring,

R₁ represents

(i) an unsubstituted or substituted un-
saturated acyclic hydrocarbon radical
or

105

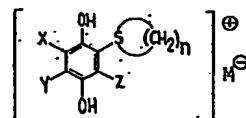
- (ii) a substituted saturated acyclic hydrocarbon radical or
 (iii) a phenyl radical substituted by lower alkoxy groups or
 5 (iv) a cycloaliphatic hydrocarbon radical;
 R_1 represents an unsubstituted or substituted saturated or unsaturated aliphatic or cycloaliphatic hydrocarbon radical or
 10 R_1 represents a phenyl radical or a phenyl radical substituted by halogen or lower alkyl and R_2 represents an unsubstituted alkyl radical of at least 2 carbon atoms; or
 15 if R_1 and R_2 represent an unsubstituted alkyl radical of from 1 to 4 carbon atoms, said radicals are not identical; or
 if of X, Y and Z at least one is not hydrogen, R_1 and R_2 represent an alkyl radical of from 1 to 4 carbon atoms, or R_1 represents an unsubstituted or substituted phenyl radical and R_2 represents a methyl group; or
 20 25 R_1 and R_2 together represent a chain of 4 to 6 methylene groups, optionally including another hetero atom in the chain and optionally including lower alkyl substituent groups; and M^\ominus represents a monovalent anion.
- 30 12. Compounds of the formula



- wherein
 X, Y and Z, independently of each other represent hydrogen, lower alkyl or halogen, provided that if 2 of the substituents X, Y and Z are other than hydrogen, the two substituents which are other than hydrogen must be identical and that if 2 of X, Y and Z are hydrogen, these are represented by X and Z,
 35 40 or
 X and Y together represent a fused ring; R_3 represents lower alkyl;

n represents an integer ranging from 3 to 6, and

M^\ominus represents a monovalent anion.
 13. Compounds of the formula



wherein

X, Y and Z represent hydrogen or
 X and Y together represent a fused benzo radical and

Z is hydrogen;
 n represents an integer ranging from 4 to 6; and

M^\ominus represents a monovalent anion.

14. Dihydroxy sulphonium salts as defined in Claims 11 and 12 when produced by a process claimed in any of Claims 1 to 10.

15. Process of producing of dihydroxyaryl sulphonium salts as claimed in Claim 1 substantially as described in any of Examples 1 to 90.

16. Dihydroxyaryl sulphonium salts as claimed in Claim 11 substantially as described in any of Examples 1-25 and 63-77.

17. Dihydroxyaryl sulphonium salts as claimed in Claims 11, and 12 substantially as described in any of Examples 26-62 and 78-90.

18. Process of producing dihydroxyaryl sulphonium salts as claimed in Claim 1 substantially as described in any of Examples 1-25 and 63-77.

19. Process of producing dihydroxyaryl sulphonium salts as claimed in Claim 1 substantially as described in any of Examples 26-62 and 78-90.

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